

## PAPER PRODUCT AND METHOD OF MAKING

### FIELD

The present invention is directed to paper having reduced cockle and water induced curl, and the method of making this paper.

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### BACKGROUND

Hardwood and softwood wood pulp fibers are used in the manufacture of printing paper and newsprint. These fibers are produced in a chemical pulping process, either sulfate or sulfite, or in a mechanical pulping process. Mechanical processes would include thermomechanical and chemithermomechanical. To form the printing paper or newsprint, these hardwood or softwood pulp fibers and wet end chemicals are mixed with water in the headbox of the paper machine to form a suspension of fibers and chemicals. The wet end chemicals may include fillers such as calcium carbonate and clay. The suspension of fibers and chemicals flow from the headbox onto a wire. The water is removed from the fibers and chemicals by both gravity and vacuum to form a wet web of pulp fibers into which the chemicals are incorporated. The chemicals are throughout the sheet. The sheet may be pressed and dried to remove more water.

Starch, optical brightener additives and surface size may be placed on surface of the sheet in a surface sizing step at the size press. Some of the materials may enter into the web if the pressure of the nip at the press is great enough.

Thereafter the web of fiber, wet end chemicals and other materials is dried by heat, calendered and rolled into rolls. The resulting product is referred to as an uncoated or lightly coated paper sheet or web.

The uncoated sheet may be coated in another application of one or more coating layers placed on the sheet in an off-line coating operation. The uncoated sheet passes through a coating station and a second drying station. It may pass through a second calendering operation. The resulting product is referred to as a coated paper sheet or web.

Uncoated or coated printing paper has a basis weight of from 16 to 180 pounds per 3300 square feet.

The application of high speed, variable printing is experiencing tremendous growth in the printing industry, displacing conventional offset printing for many applications. A digital printing technology such as web-fed ink jet printing presents new and different challenges for the paper maker as the optimum surface physics and

chemistry of paper for these printers are very different than those required for conventional offset inks.

High speed, ink jet printing is exceptionally challenging because it employs aqueous inks and a great deal of water is placed on the paper surface during the printing process. In the process, these water based inks may be applied at high coverage at paper speeds of 500-1,000 ft. per minute. It is difficult to completely dry the paper before the paper leaves the printer. If uncoated paper is used, the water from the ink penetrates the sheet and disrupts the bonding between the paper fibers. This creates a deformation of the paper surface, which results in unacceptable curling, cockling, or puckering of the printed paper.

Standard desk top ink jet printers are increasing in speed and some of the same challenges are found when printing with these printers because of the water placed on the paper and the difficulty of completely drying the paper before it leaves the printer.

Wide printers have similar challenges because of the amount of ink and water placed on the paper.

Because of these factors, special papers are used when the print job requires high levels of ink coverage. These special papers are coated with water-absorbent silica or swellable gel materials such as polyvinyl pyrrolidone, or combinations of these materials. Typically, these materials are applied by an off-line coating operation. The price of these materials and the off-line application significantly increases the cost of paper for these applications.

The optical density of the printed image is also of primary concern for many print jobs as high levels of ink are required to provide vivid, robust colors. This is known as high optical density. Uncoated papers are limited in the amount of ink they can tolerate because of their tendency to curl and cockle. Thus more expensive coated papers are generally required when high optical densities are needed.

#### SUMMARY

The present invention is directed to an uncoated paper usable with ink having a water content and which has a maximum Cockle Value of 0.25. The Cockle Value is used to determine the amount of cockle or water induced curl in the paper. An embodiment of the invention is an uncoated paper having a paper basis weight of 16 to 60 pounds per 3300 square feet and a maximum Cockle Value of 0.25.

An embodiment of the invention is a paper that has been treated with at least 50 pounds per ton of paper with a material that is capable of being added at the size press,

blade coater or by a spray before the heated drying section. The material is water soluble, is highly concentrated during application, has low viscosity and low hygroscopicity. Water soluble means a compound that is soluble to concentrations of 20-50% of the total weight of the solution at room temperature or at temperatures of 50° C. or less. Highly concentrated means the weight or concentration of the material is 20-50% of the weight of the solution. Low viscosity means viscosities of 200 centipoises (cps) or less when the weight or concentration of the material is 20-50% of the weight of the solution. Low hygroscopicity means the dried material will take up only a small amount of water in high humidity conditions. Another embodiment is a paper that has been treated with at least 75 pounds of the material per ton of paper. Another embodiment is a printing paper that has been treated with up to 250 pounds of the material per ton of paper. Another embodiment is a paper that has been treated with up to 300 pounds of the material per ton of paper.

In one embodiment of the invention the material is a disaccharide. In another embodiment of the invention the material is a monosaccharide. In another embodiment of the invention the material is a urea. In another embodiment of the invention the material is a mono-citrate or di-citrate.

In another embodiment of the invention the material is combined with starch, latex, polyvinyl alcohol, styrene acrylic acid or an ester and the low viscosity of the additive can be maintained.

#### BRIEF SUMMARY OF THE DRAWINGS

Figures 1-2 are digital Images of untreated commercial paper using LANDCO Low Angle Light:

Figures 3-4 are digital Images of sucrose treated paper using LANDCO Low Angle Light:

Figures 5-10 are digital images of treated and untreated pape from the second side cockle test method.

Figure 11 is a graph showing the coefficient of variation of treated and untreated samples.

Figure 12 is a drawing of the work station for carrying out the second side cockle test method.

Figure 13 is a schematic diagram of a paper machine.

## DETAILED DESCRIPTION

The present invention is directed to an uncoated or lightly coated paper which may be used for printing on ink jet printers and which has a maximum Cockle Value of 0.25 after such printing. It is also directed to an uncoated or lightly coated wide

5. printing paper used with ink jet printers which has a maximum Cockle Value of 0.25

A quantitative test has been developed to determine the curl and cockle of paper. It replaces the subjective test of viewing the paper to determine whether there was curl and cockle and the amount of curl and cockle. This prior subjective test also determined whether a sheet of paper had sufficient treatment. The quantitative test is  
10 the second side cockle test method.

The second side cockle test method is used to evaluate the amount of cockle that an inkjet print, at an ink application level of 5.9 grams/square meter, produces in the unprinted or second side of a paper printed with a block print. The present test used a Scitex Test Cockle Form Print. The unprinted side of the inkjet print is  
15 illuminated using low angle ( $15^0$ ) lighting. A digital image is made of the cockled area on the unprinted side associated with a 3.5 by 3.5 inch half-tone printed square on the printed side of the sample. The image is then evaluated to determine the amount of second side cockle.

The apparatus used for the second side cockle test method is shown in  
20 Figure 12. It includes a test platform 10, a Kodak® megapixels 8-bit digital camera 12, and a Dedolight® light 14. The camera 12 is mounted above surface 16 of the test platform 10 and at  $90^0$  to the surface 16 of the test platform 10. The camera is aimed directly at the center of the surface 16 of the platform. The Dedolight light 14 is mounted at an angle of  $15^0$  to the surface 16 and also aimed at the center of  
25 the surface 16. Mathworks, Inc. Matlab® computer software is used to analyze the images.

The samples of paper to be tested are printed on one side with a Scitex Test Cockle Form using an inkjet printer and inkjet ink. In the following tests a Hewlett Packard ink jet printer HP560C was used. The ink used was Scitex Ink 2002 and  
30 the ink application level was 5.9 g/square meter. The ink should be a water based ink. The paper was handled carefully so as not to crease or wrinkle the paper because creases or wrinkles would be analyzed as cockle.

The settings of the camera 12 were adjusted to a pixel resolution of 100 microns/pixel and an f-stop of F8. The camera control was on Fixed and the image

centering was at 127. The Dedolight light 14 was adjusted for uniform low angle lighting. All lighting was from the Delolight light 14. Other room lights were turned off.

5 The paper sample 18 was placed on the surface 16 of the test stand 10 with the unprinted side of the paper turned to the camera and facing up. The 3.5 by 3.5 inch cockle area was centered in the camera field of view with the light aimed at the center of the cockle area. The camera's exposure was adjusted until the average image pixel value was 127. The image was collected and saved to a disk.

This process was repeated for each sample.

10 The images were analyzed using the Mathworks, Inc. Matlab® computer software. Version 6, release 13 was used. The image is read into the program and smoothed with a 5x5 median filter to remove high frequency noise. The mean, standard deviation and coefficient of variation were calculated for each row and column. The larger of the maximum row coefficient of variability and maximum  
15 column coefficient of variability is taken as the sample Cockle Value. The program is evaluating the differences between the light and dark areas of the image and determining the variability.

Cockle Value means the cockle value determined by this test.

An embodiment is an uncoated paper that has been treated with at least 50  
20 pounds per ton of paper with a material that is water soluble, is highly concentrated during application, has low viscosity and low hygroscopicity to reduce curl, cockle or other deformation after printing with high levels of ink jet ink as compared to uncoated paper. The maximum Cockle Value of the treated printing paper is 0.25. A ton is defined here as 2000 pounds. Water soluble means a compound that is soluble to  
25 concentrations of 20-50% of the total weight of the solution at room temperature or at temperatures of 50° C. or less. Highly concentrated means concentrations of 20-50% of the weight of the solution. Low viscosity means viscosities of 200 centipoises or less at concentrations of 20-50% of the weight of the solution. Low hygroscopicity means the dried material will not take up water in high humidity conditions.

30 In another embodiment of the invention at least 75 pounds of material per ton of paper is used. In another embodiment of the invention as much as 300 pounds of the material per ton of paper may be used. In another embodiment as much as 250 pounds of the material per ton of paper may be used.

The material is applied at the size press or the blade coater. It may be applied using a puddle, gate roll or metered size press, or a knife or blade coater. In one embodiment the material may be applied in a solution containing at least 20% by weight of material. In another embodiment the material may be applied in a solution  
5 containing 20 to 50% by weight of the material.

In one embodiment of the invention disaccharides may be used as the material. Disaccharides such as sucrose and maltose can be used. Any disaccharide having the properties noted above can be used. Many disaccharides have viscosities below 200 centipoise (cps.) at concentrations 20 to 50% of the weight of the solution.

10 Another embodiment of the invention may use monosaccharides. Monosaccharides such as glucose or mannose can be used. Many monosaccharides have viscosities below 200 centipoise (cps.) at concentrations 20 to 50% of the weight of the solution.

A material such as corn syrup may also be used.

15 Hygroscopicities and solubilities of certain polyols are listed in table 1. From this table it can be seen that malitol, lacitol monohydrate and erythritol have the desired characteristics.

**Table 1**

<b>Polyol</b>	<b>Solubility at 25°C g/100g H<sub>2</sub>O</b>	<b>Degree of hygroscopicity % ERH @ 20°C</b>
Mannitol	22g	very low
Malitol	175g	low
Lacitol monohydrate	140g	low
Anhydrous isomalt	39g	very low
Erythritol	61g	very low
sucrose	185g	low
maltose	70g	medium

20 **Example 1.**

Paper containing sucrose, starch, and surface size:

The percentages in this example are weight percentages.

A 60 gm./m<sup>2</sup> unsized paper was used for each of the samples in this example.

A control sample of paper was coated in a laboratory size press with ethylated starch at 12% concentration. Both side of the paper were coated to a coat weight of 40 pounds of starch per ton of paper per side. This is typical of most uncoated paper grades (Formula I).

5 One sample of paper was treated in a lab size press with a solution containing a concentration of 35% sucrose, 5% ethylated starch and 1% surface size (Hercules IJP). Both side of the paper were coated to a coat weight of 105 pounds of material per ton of paper per side (Formula II). The amount of sucrose was about 90 pounds per ton of paper per side.

10 A second sample was prepared with a solution containing a concentration of 40% sucrose, 5% ethylated starch and 1% surface size (Hercules IJP). Both sides of the paper were coated to a coat weight of 112.5 pounds of material per ton of paper per side (Formula III). The amount of sucrose was about 98 pounds per ton of paper per side.

15 Each of the sheets were then dried and conditioned at 50% R.H..

One set of the sheets was printed using an HP 560 printer and Scitex High Speed ink jet ink. The image was a 3" x 3" square, printed at 60% density, using Corel Draw, Version 10.

20 The printed sheets were then placed in a darkroom, face down and viewed under a LANDSCO triple-bulb, low angle light. The degree of curl and cockle were then visually estimated. The results are given in Table 2. 100% is the base case for a starch control. The others were judged against the starch control.

**Table 2**

<b>Formula</b>	<b>Degree of Curl / Cockle: Scitex ink</b>
Formula I	100%
Formula II	<10%
Formula III	<5%

25 Two commercial paper products A and B, printed with a HP 560 printer using Scitex high speed ink jet ink were digitally recorded with a SONY Mavica digital camera, under low angle light. These photographs are Figures 1 and 2. The Formula II and Formula III sheets from Example 1 were also digitally recorded with a SONY Mavica digital camera, under the same low angle light. These photographs are Figures

3 and 4. Figure 3 shows the Formula II sheet from Example 1; Figure 4 shows the Formula III sheet from Example 1. The reduction in curl and cockle with high levels of sucrose is easily observed by comparing Figures 1 and 2 with Figures 3 and 4.

Another embodiment of the invention may use urea as the material. This material has the desired characteristics.

Example 2.

60 gm./m<sup>2</sup> unsized paper was used as the base paper for the sheets in this example.

The percentages in this example are weight percentages.

The Formula 1 control samples from Example 1 were also used as the control samples in this example.

A sample of paper was treated in a lab size press with a solution containing a concentration of 40% urea, 5% ethylated starch and 1% surface size (Hercules IJP). Both side of the paper were coated to a coat weight of 101.5 pounds of material per ton of paper per side (Formula IV). The amount of urea was about 88 pounds per ton of paper per side.

The sheets were then dried and conditioned at 50% R.H..

The sheets were printed using an HP 560 printer and Scitex High Speed ink jet ink. The sheets were then evaluated for curl and cockle, using the same technique as in Example 1.

The results are shown in Table 3.

**Table 3**

<b>Formula</b>	<b>Degree of Curl / Cockle: Scitex ink</b>
Formula I	100%
Formula IV	<5%

Another embodiment of the invention uses a salt of citric acid as the material.

Example 3.

60 gm./m<sup>2</sup> unsized paper was used as the base paper for the sheets in this example.

The percentages in this example are weight percentages.

The Formula 1 control samples from Example 1 were also used as the control samples in this example.



A sample of paper was treated in a lab size press with a solution containing a concentration a 25% of the monosodium salt of citric acid (monosodium citrate), heated to 50 degrees C. Both side of the paper were coated to a coat weight of 37.5 pounds of material per ton of paper per side (Formula V).

5 The sheets were then dried and conditioned at 50% R.H..

The sheets were printed using an HP 560 printer and Scitex High Speed ink jet ink. The sheets were then evaluated for curl and cockle, using the same technique as in Example 1. The sheets were also tested for water fastness via submersion in water for 60 seconds and the ink dye was completely immobilized by the salt.

10 The results are shown in Table 4.

**Table 4**

<b>Formula</b>	<b>Degree of Curl / Cockle: Scitex ink</b>	<b>Water Fastness</b>
Formula I	100%	Poor
Formula V	<5%	Excellent

It is believed that both the mono or di salts of citric acid provide water fastness.

Water fast means the ability of ink to remain intact when exposed to water or  
15 moisture. Water fast inks do not bleed. Water based inks must be treated to be water fast.

Water fastness is typically obtained with a nitrogen-containing organic compound of a cationic nature and functions by precipitating the dye in the ink, rendering it immobile, when exposed to moisture after printing. Unfortunately, these  
20 types of materials are incompatible with anionic fluorescent whitening agents, optical brighteners, which are typically applied at the size press to brighten paper. As such, these types of additives reduce the overall paper brightness, often times to levels below customer acceptance.

Monosodium citrate maintains the brightness of the paper while providing  
25 water fastness.

#### Example 4

Samples were also evaluated using the second side cockle test method.

The percentage shown are weight percentages.

60 gm./m2 unsized paper was used as the base paper for the sheets in this  
30 example.

The Formula 1 control samples from Example 1 were also used as the control samples in this example.

A second sample was prepared with a solution containing a concentration of 44% sucrose, 5% ethylated starch and 1% surface size (Hercules IJP). Both sides of the paper were coated to a coat weight of 105 pounds of material per ton of paper per side. The amount of sucrose was 92.4 pounds per ton of paper per side.

A third sample of paper was treated in a lab size press with a solution containing a concentration of 35% urea, 5% ethylated starch and 1% surface size (Hercules IJP). These percentages are weight percentages. Both side of the paper were coated to a coat weight of 101.5 pounds of material per ton of paper per side. The amount of urea was about 87 pounds per ton of paper per side.

A fourth sample of paper was treated in a lab size press with a solution containing a concentration a 25% of the monosodium salt of citric acid, heated to 50 degrees C. This percentage is a weight percentage. Both side of the paper were coated to a net coat weight of 37.5 pounds of material per ton of paper per side. The amount of citrate was 37.5 pounds per ton of paper per side.

Two commercial papers were added to the study.

The samples were evaluated both visually and using the second side cockle test method. The image evaluation test correlated well with the visual observation.

The results are given in Table 5 and in Figure 11.

**Table 5**

Formula	Sample Designation	Visual Rank	Subjective Value	Cockle Value
5% Starch, 44% Sucrose	Figure 5	1 – 2	Acceptable	0.2060
5% Starch, 35% Urea	Figure 6	1 – 2	Acceptable	0.2127
25% mono sodium salt of citric acid	Figure 7	3	Acceptable	0.2296
12% Starch control	Figure 8	4	Unacceptable	0.2658
First Choice <sup>TM</sup>	Figure 9	5	Unacceptable	0.2851
CI-2000 <sup>TM</sup>	Figure 10	6	Unacceptable	0.3211

It was determined that paper sheets having Cockle values of 0.25 or less were acceptable.

Figure 13 is a schematic drawing of a paper machine. Wood pulp fiber furnish and wet end chemicals are mixed with water in a headbox 20 to form a slurry. The

slurry exits the headbox through a slice 22 onto a wire 24. The water in the slurry drains from the wire. A vacuum chest 26 is also used to draw water from the slurry to form a wet paper web. The web is carried through press rolls 28 and a drier 30 that remove additional water.

5 Additional size press chemicals or materials are placed on the wet paper web at the size press 32. The size press may be a horizontal type with the rolls horizontally aligned, a vertical type with the rolls vertically aligned. The materials may be placed on the web from the rolls or from a puddle between the rolls. The web may, in some instances, be coated with material by the spraying apparatus 34. The materials  
10 described in the various embodiments in the present application would also be applied at the size press 32 or the spraying apparatus 34.

The paper web then passes through a drying section 36. The drying is usually done by steam heated drier cans through which the paper web is threaded. The paper is then calendered by calender rolls 38 and rolled into paper rolls at the winder 40. The  
15 resulting product is known as uncoated paper.

This is the product of the present invention. Additional expensive off-machine coatings would not be required to provide a paper that has a maximum Cockle Value of 0.25.

Those skilled in the art will note that various changes may be made in the  
20 embodiments described herein without departing from the spirit and scope of the present invention.